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(54) Improved lubricating oil composition.

(57) A lubricating composition having improved anti-wear properties comprises:

A. a lubricating oil basestock;
B. a metal phosphate;
C. a metal carbamate; and
D. an alkyl hydroxy-aryl sulfide.

The metal phosphate is preferably a dialkylphosphate, zinc compounds being especially suitable. From about 0.1 to about 1.0 wt.% (based on the basestock) is preferred.

The metal carbamate is preferably a dithiocarbamate, more especially zinc compounds. From about 0.1 to about 1.3 wt.% is preferred.

The sulfide is preferably an alkyl phenol sulfide, for example, nonyl phenol sulfide. From about 0.2 to about 2 wt.% is preferred.

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IMPROVED LUBRICATING OIL COMPOSITION

The present invention relates to a lubricating oil composition (herein also called lube oil composition) and more especially to one having a reduced phosphorus content while exhibiting satisfactory anti-wear and friction reducing properties.

In current lube oil formulations for internal combustion engines, phosphorus-containing compounds such as zinc dialkyldithiophosphate (ZDDP), are added to the lube oil formulation to provide improved anti-wear properties. However, it has been found that phosphorus from phosphorus-containing compounds becomes deposited on the catalyst in catalytic converters, thereby decreasing the efficiency of catalytic converters over time. As a result, vehicle manufacturers have recommended that engine oil contain reduced phosphorus contents. At the present time automotive lube oils typically contain a maximum of about 0.10 to about 0.14 weight percent phosphorus. To reduce the rate at which catalytic converters become fouled by phosphorus, it would be advantageous to reduce the phosphorus content of the lube oils to about 0.08 weight percent, or lower.

The use of dialkyldithiocarbamates in lube oils is known. U.S. Patent No. 4,178,258 discloses the use of zinc dialkyldithiophosphate (ZDDP) and a wear inhibiting amount molybdenum bis(dialkyldithiocarbamate). This patent also discloses the addition of sulfurized calcium phenates in the lube oil formulation. However, the addition of sulfurized calcium

phenates to a lube oil is not desirable because it may reduce the fuel economy and anti-rust properties of the lube oil.

U.S. Patent No. 3,513,094 also discloses the use of metal dithiocarbamates in lube oils. This patent discloses the use of the metal dithiocarbamates in combination with antimony dihydrocarbyldithioate. This patent also discloses the use of sulfurized sperm oil.

U.S. Patent No. 3,923,669 discloses the use of zinc dialkyldithiophosphate and a neutral barium salt of a petroleum sulfonate diaryldithiocarbamate. The use of neutral barium salts of a petroleum sulfonate is not desirable because of the toxicity of barium.

Japanese Patent Publication J54,113,604 discloses the combination of molybdenum sulfide-oxide, ZDDP and dialkyldithiocarbamate in a lubricant for internal combustion engines.

It is desirable to decrease the concentration of phosphate-containing compounds, such as zinc dialkyldithiophosphate, present in lubricating oil to thereby decrease the rate at which phosphates become deposited on the catalyst.

It also is desirable to provide a lube oil having anti-wear and friction reducing properties comparable to presently available lube oils while also having a reduced phosphorus content.

In accordance with the present invention, a lubricating oil composition having improved properties comprises:

A. a major amount of a lubricating oil basestock; and minor amounts of

B. a metal phosphate;

C. a metal carbamate; and,

D. an alkyl hydroxy-aryl sulfide.

The concentration of the metal phosphate, preferably a metal dithiophosphate (MDTP), may be limited to a range of about 0.1 or 0.2, to about 1.0, weight percent of the lube oil so that the concentration of phosphorus is less than about 0.08 weight percent, preferably 0.05 weight percent or less of the lube oil.

The present invention also is directed at a method for improving the anti-wear properties of a lube oil basestock comprising the addition to the basestock of an effective amount of:

A. a metal phosphate;

B. a metal carbamate; and,

C. an alkyl hydroxy-aryl sulfide.

In a preferred embodiment the metal salt is a metal dialkyldithiophosphate salt including a Group IB, IIB, VI^B or VIIIB metal with zinc, nickel and copper being particularly preferred. The alkyl groups preferably comprise C_3-C_{10} alkyls. The concentration of the metal dialkyldithiophosphate salt relative to the basestock ranges between about 0.1 and about 1.0 weight percent, preferably between about 0.3 and about 0.6 weight percent.

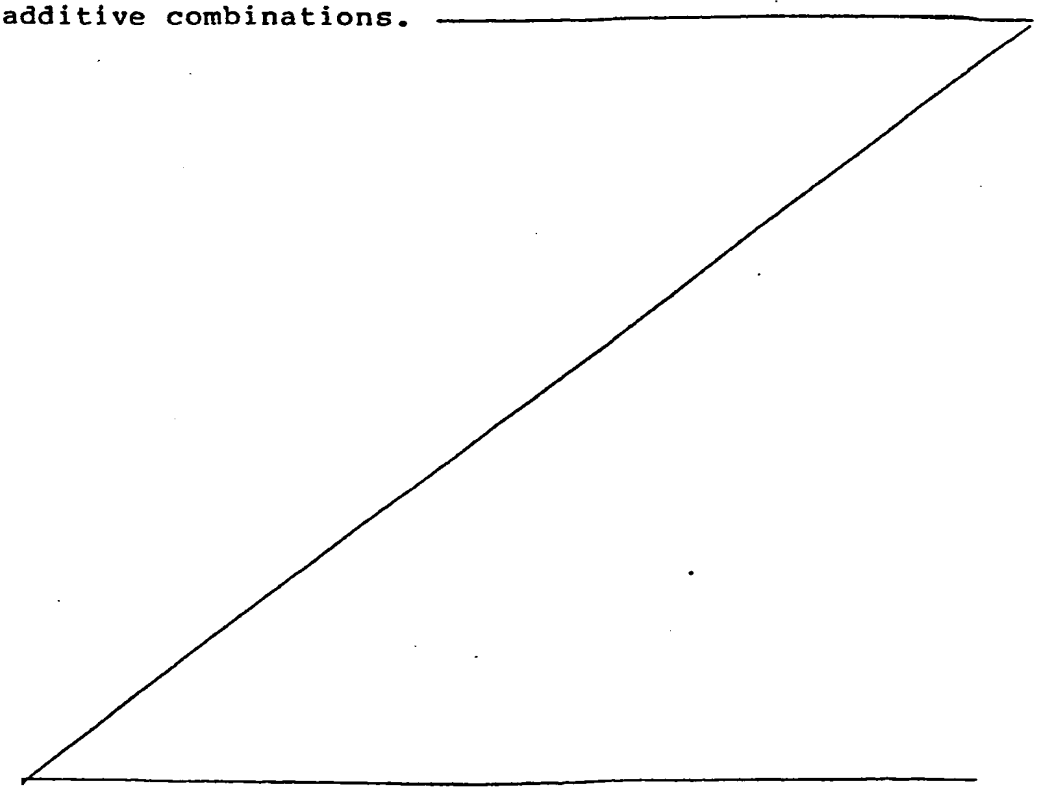
The metal carbamate preferably comprises a metal dithiocarbamate wherein the metal is selected from Groups IB, IIB, VIB, VIIIB of the Periodic Table and mixtures thereof. Preferred metals include zinc, iron and nickel, with zinc being particularly preferred. The concentration of the metal dithiocarbamate may range between about 0.1 and about 1.3 weight percent, based upon the basestock content, preferably between about 0.2 and about 0.8 weight percent.

The alkyl hydroxy-aryl sulfide preferably comprises an alkyl phenol sulfide where the alkyl group preferably ranges between about C_6 and about C_{18} with a nonyl phenol sulfide being particularly prefer-

red. The concentration of the alkyl hydroxy aryl sulfide may range between about 0.2 and about 2.0 weight percent, based upon the basestock content, preferably between about 0.4 and about 0.8 weight percent.

BRIEF DESCRIPTION OF THE DRAWINGS

The Figure represents a plot of average cam lobe wear as a function of time for varying lube oil additive combinations.



The basestock utilized in the present invention is not critical and may be selected to achieve the desired final properties of the lube oil. The basestock may be natural or synthetic or both.

The metal phosphate of the present invention preferably comprises a metal dialkyldithiophosphate wherein the metal is selected from the group consisting

of Group IB, IIB, VIB, VIIIB and mixtures thereof, with nickel, copper and zinc being particularly preferred. The alkyl groups preferably comprise C_3-C_{10} alkyls. Particularly preferred compounds are zinc dialkyldithiophosphates. These compounds and the methods for making same are well-known by those skilled in the art. The concentration of the metal dialkyldithiophosphate may range between about 0.1 and about 1.0 weight percent based upon the basestock content, preferably between about 0.3 and about 0.6 weight percent.

The metal carbamate preferably comprises a metal dithiocarbamate where the metal preferably is selected from the group consisting of Group IB, IIB, VIIB and VIIIB. Preferred metals include zinc, nickel and iron, with zinc dithiocarbamate being particularly preferred. The concentration of the metal carbamate may range between about 0.1 and about 1.3 weight percent, based upon the basestock content, preferably between about 0.2 and about 0.8 weight percent. The zinc dithiocarbamate (ZDTC) is readily available as an article of commerce.

The alkyl hydroxy-aryl sulfide preferably comprises an alkyl phenol sulfide in which the alkyl groups preferably range between about C_6 and C_{18}. Nonyl phenol sulfide is a particularly preferred compound. The concentration of the alkyl hydroxy-aryl sulfide may range between about 0.2 and about 2.0 weight percent, based upon the basestock content, preferably between about 0.4 and about 0.8 weight percent. Nonyl phenol sulfide (NPS) is well-known by those skilled in the art and is readily obtainable as an article of commerce.

The following comparative examples and examples demonstrate the utility of the present invention. The tests comprised valve train wear tests utilizing a Ford 2.3 liter engine with the pistons and connecting rods removed. The engine was driven with an 11.2 KW (15 horsepower) DC drive motor through a 1.2 timing belt drive. The engine was equipped with Oldsmobile valve springs (146.5-148.3 KG) to increase the load between the cam lobes and the followers. Both oil and coolant circulation were accomplished by use of the engine mounted pumps. All test runs were made at 90°C oil temperature, 90°C coolant temperature, approximately 331 kPa oil pressure and an engine speed of 1,000 plus or minus 6 rpm.

During operation, wear is generated on the lobes of the cam shaft and followers due to the sliding contact. As in the sequence V-D test described in ASTM Test No. STP 315H-Part 3, the disclosure of which is incorporated herein by reference, wear is defined as the reduction of the head-to-toe measurement at the point of maximum lift on the cam shaft. A pre-measured cam shaft is measured at various time intervals during the test to establish the reduction in the head-to-toe distance, i.e. the degree of wear. The tests were conducted with a commercially available lubricating oil from which the anti-wear additive had been removed and which were modified somewhat to simulate actual used oil conditions.

Comparative Example 1

In this test 0.41 weight percent of zinc dialkyldithiophosphate and 0.80 weight percent of zinc dithiocarbamate were added to the lube oil noted above.

The engine was run for only 40 hours to prevent engine seizure due to high wear which had been detected after 20 hours of operation. The average cam lobe wear was 29.5 micrometers (μm) and 95.4 μm after 20 and 40 hours, respectively.

Comparative Example 2

A test similar to that described in Comparative Example 1 was run in which the lube oil contained 0.41 weight percent of ZDDP and 0.80 weight percent of nonyl phenol sulfide. Again, the test was run for 40 hours after which the cam lobe was measured. The average cam lobe wear was 36 μm and 96.2 μm after 20 and 40 hours of testing, respectively.

Comparative Example 3

This Comparative Example was conducted similar to that of Comparative Example 1, but in this test 0.80 weight percent of zinc dithiocarbamate and 0.41 weight percent nonyl phenol sulfide were added to the lube oil. The average cam lube wear was 39.9 μm and 106 μm after 20 and 40, respectively.

Example 1

This test was conducted in a manner similar to that described hereinabove for the Comparative Examples. However, in this test the lube oil had added thereto all three of the above-noted additives, 0.41 weight percent zinc dialkyldithiophosphate, 0.30 weight percent zinc dithiocarbamate and 0.50 weight percent nonyl phenol sulfide. The average cam lobe wear was only 9.2 μm, 10.6 μm, 11.6 μm and 11.6 μm after 20, 40, 60 and 80 hours of testing, respectively.

The data obtained in Comparative Examples 1-3 and in Example 1 are plotted on Figure 1. The average cam lobe wear in micrometers is plotted as a function of time. From a review of the data presented in Figure 1 and in Table 1 it can be seen that the combination of zinc dialkyldithiophosphate, zinc dithiocarbamate and nonyl phenol sulfide resulted in lower cam lobe wear than an equal weight of only two of the three additives.

TABLE I

Test Reference	Additive Concentration, Wt.% ZDDP	ZDTC	NPS	Total Additive Concentration, Wt.%	Average Cam Lobe Wear, Micrometers (μm) 20 Hr	40 Hr	60 Hr	80 Hr
Comp. e.g. 1	0.41	0.80	0	1.21	29.5	95.4	--	--
Comp. e.g. 2	0.41	0	0.8	1.21	36.0	96.2	--	--
Comp. e.g. 3	0	0.80	0.41	1.21	39.9	106.0	--	--
Example 1	0.41	0.30	0.5	1.21	9.2	10.6	11.6	11.6

CLAIMS:

1. A lubricating oil composition comprising:

A. a lubricating oil basestock;
B. a metal phosphate;
C. a metal carbamate; and
D. an alkyl hydroxyl-aryl sulfide.

2. A composition as claimed in claim 1, wherein the phosphate is of a metal selected from Groups IB, IIB, VIB, VIIIB and mixtures thereof.

3. A composition as claimed in claim 2, wherein the metal phosphate comprises a metal alkylphosphate, preferably zinc diakyl-dithiophosphate.

4. A composition as claimed in claim 2 or claim 3, wherein the metal is selected from zinc, nickel, copper and mixtures thereof.

5. A composition as claimed in any preceding claim, wherein the metal carbamate comprises a metal dithiocarbamate, preferably zinc dithiocarbamate.

6. A composition as claimed in any preceding claim, wherein the alkyl hydroxy-aryl sulfide comprises an alkyl phenol sulfide, preferably nonyl phenol sulfide.

7. A composition as claimed in any preceding claim containing, based on the weight of the basestock, about 0.1 to about 1.0 wt.%, preferably about 0.3 to about 0.6 wt.%, of said metal phosphate, preferably metal dialkyldithiophosphate.

8. A composition as claimed in any preceding claim containing, based on the weight of the basestock, about 0.1 to about 1.3 wt.%, preferably about 0.2 to about 0.8 wt.%, of said metal dithiocarbamate.

9. A composition as claimed in any preceding claim containing, based on the weight of the basestock, about 0.2 to about 2.0 wt.% preferably about 0.4 to about 0.8 wt.% of said alkyl hydroxy-aryl sulfide.

10. A method of improving the anti-wear properties of a lubricating oil basestock, comprising the addition to the basestock of an effective amount of:

A. a metal phosphate;
B. a metal carbamate; and
C. an alkyl hydroxy-aryl sulfide; each of A, B and C being as defined in any preceding claim.

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FIG. 1